

PURIFICATION OF CARBON NANOTUBES FROM CATHODE DEPOSIT BY MEANS OF DIFFERENT OXIDATION RATES

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Abstract

Two purification methods of nanotubes from a cathode deposit by an arc plasma were conducted by means of different oxidation rates of various graphites. One was chemical and the other physical method. Both could purify nanotubes at their optimum conditions. In the former, the catalytic oxidation was used of graphite materials by copper. Copper supported graphite was prepared by the intercalation of copper chloride and by the reduction to metal copper. The catalytic oxidation decomposed the graphite at 773 K and less. The temperature was significantly lower than the oxidation temperature former reported of graphite, which enabled purification. In the latter, dispersion, comminution and filtration of a cathode deposit in ethanol were used to separate coarse graphite. The rate of weight loss by oxidation increased with the decrease of size of the graphite. Nanotubes were more slowly oxidized from the edges than the graphite of the same size. This could purify nanotubes.

1. Introduction

Carbon nanotubes were first observed by Iijima¹⁾ in cathode deposits produced by an arc plasma method. They are completely novel carbon materials which have the property of either metal or semi-conductor according to the diameter and helical pitch²⁾. Carbon nanotubes are also expected to have about two order higher fracture strength than that of commercial carbon fibers due to few defects in carbon crystal structures. Other carbon materials like graphite and amorphous carbon existed together with carbon nanotubes in the cathode deposit. Different from C60, carbon nanotubes are not dissolved in any organic solvent. Carbon nanotubes have to be purified from these carbon materials not only to analyze the properties but also to utilize the unique properties for industrial applications.

Some methods³⁾⁻⁶⁾ were proposed for the purification. These methods were based on oxidation methods. But carbon nanotubes and other carbon materials in cathode deposits are not considered that they have much different oxidation rates. Some process was inevitable to enlarge the difference of oxidation rates between carbon nanotubes and the other carbon materials before oxidation. Two such methods were developed in our group; one was chemical, the other physical method.

2. Experimental procedure

2.1 Sample

In chemical method, graphite powder (Nippon Carbon Co., SAD-4) was used for a model graphite. The diameter ranges from #100 to #325 (about 44-149 μm). Crude nanotubes, i.e. as-prepared cathode deposits were purchased from Shinku Yakin Co. or were prepared by an arc plasma in our laboratory. The weight percentage of nanotubes contained in the cathode deposit was not known.

2.2 Basic idea of both methods and procedures

Chemical method The chemical method is based on the concept that graphite intercalation compounds (GIC) are not synthesized in the case of carbon nanotubes because of the rigid structure of carbon nanotubes. Some metals like copper, molybdenum and so on catalytically oxidize graphite⁷⁾ at a rather low temperature. When graphite materials in cathode deposits intercalate such metal, for instance copper, carbon nanotubes are expected to be purified at a rather lower temperature. Fig.1 is the procedure of chemical purification method. In our experiment copper was selected as a catalyst. Copper chloride-intercalated graphite ($\text{CuCl}_2\text{-GIC}$) was prepared, followed by the reduction of chloride to metal copper, because copper-intercalated graphite was not obtained directly and chloride-intercalated graphite was stable in the air. Copper chloride-intercalated graphite was reduced either by gas phase containing hydrogen at 773 K for 1 hour or by metal lithium in THF containing naphthalene at room temperature for 1 week. Thus prepared graphite is hereafter called as copper supported graphite.

Physical method Basic idea is that the apparent oxidation rate of carbon material depends on the diameter of the material. There were various kinds of carbon materials in as-prepared cathode deposits, some of which were rather coarse graphite particles with lower oxidation rate than carbon nanotubes. Only very small portion of existing carbon nanotubes would survive when the as-prepared cathode deposits containing carbon nanotubes, amorphous carbon and graphite materials, were oxidized all together. Separation process is necessary of rather coarse carbon materials, i.e. coarse graphite from the as-prepared cathode deposit before oxidation process. Schematic procedure of the physical method is shown in Fig.2. Dispersion in methanol, classification by centrifugal forces and comminution in methanol of

cathode deposits were utilized to separate graphite particles with larger Stokes' diameter than carbon nanotubes. Then purified carbon nanotubes would be obtained by higher oxidation rate of the cathode deposits with equal and smaller Stokes' diameter than carbon nanotubes.

2.3 Characterization

Particle size distribution was measured by centrifugal settling photoextinction method(Shimadzu SA-CP3).

Thermogravimetric analyzer(Shinku rikou, TGD 9600) measured the oxidation rate of the cathode deposits remaining in each separation step in the physical method and of graphite and copper supported graphite in the chemical method. The sample weight was usually ca. 10 mg, but was ca. 2 mg in the case of the cathode deposit remaining in each separation step in the physical method. Temperature was raised at a rate of 10 K/m.

SEM(Hitachi, S-800 with EDX) was used for observation and element analysis of cathode deposits and of purified carbon nanotubes.

XRD(Philips PW1800) was used to measure the crystal structure of cathode deposit, graphite, copper chloride-intercalated graphite and copper supported graphite.

Oxidation was also conducted with Thermogravimetric analyzer.

3. Results and discussions

3.1 Chemical method

Copper chloride-intercalated graphite(CuCl₂-GIC) and copper supported graphite were identified by XRD profiles as shown in Fig.3. Oxidation rate measured by Thermogravimetry (TG.) is depicted in Fig.4. Copper supported graphite was oxidized at a considerable rate at the low temperature of 673 K.

Copper particles in the cathode deposits after the reduction by hydrogen seemed a little larger than those by metal lithium. The reduction by metal lithium was therefore considered better for the purification of crude nanotubes.

Oxidation was examined from 673 to 873 K. Fig.5 shows the photographs at the oxidation temperature of 773 K. Even at the low temperature of 673 K carbon nanotubes could also be purified. The temperature was ca. 350 K lower than that of Ebbesen's method. The chemical method needs some reagents and takes time, but is very easy to be conducted.

3.2 Physical method

Figs 6 and 7 show the particle size distribution and oxidation rate of as-prepared cathode deposit and the cathode deposit remaining in each separation step. Apparent oxidation rate increased with the decrease of the particle size distribution of the remaining cathode deposit. The apparent activation energy also decreased with the decrease of the particle size distribution.

Purified carbon nanotubes are shown in Fig.8, which shows this method could separate graphite from the as-prepared cathode deposit. The oxidation temperature of 823 K. The temperature was about 200 K lower than that of Ebbesen's method. One of the defects in this method is rather tedious and needs skill.

4. Conclusion

Two purification methods were proposed of carbon nanotubes from as-prepared cathode deposits; one was chemical, the other physical method. Followings are the results induced.

- (1) Both methods purified carbon nanotubes from as-prepared cathode deposit.
- (2) The oxidation temperature was greatly lower than that of Ebbesen's method; ca. 350 K in chemical method and 200 K in physical method.
- (3) Any process was inevitable to enlarge the difference of oxidation rate between carbon nanotubes and the other carbon materials containing in as-prepared cathode deposit.
- (4) Optimization of the two methods is still necessary according to the varying property of as-prepared cathode deposit.

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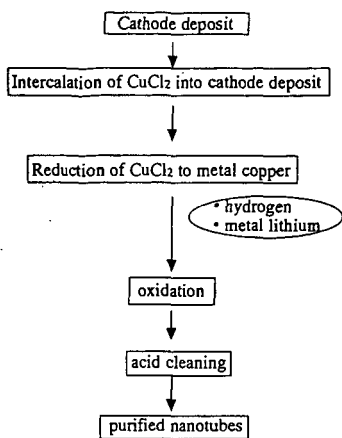


Fig.1 Procedure of chemical method

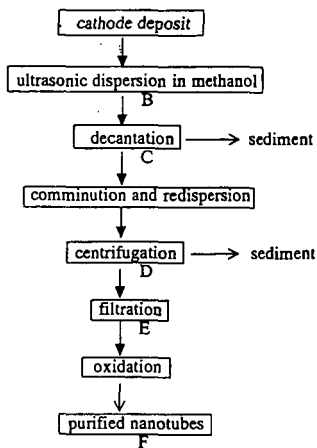


Fig.2 Procedure of physical method

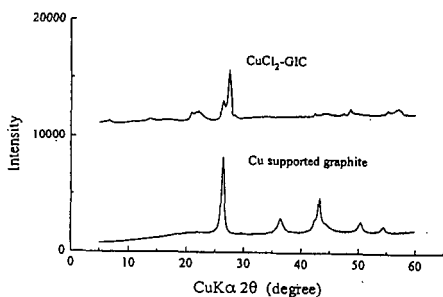


Fig.3 XRD profiles of CuCl₂-intercalated graphite and Cu supported graphite

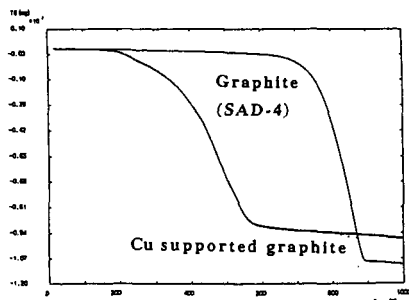


Fig.4 TG analysis of graphite(SAD-4) and Cu supported graphite

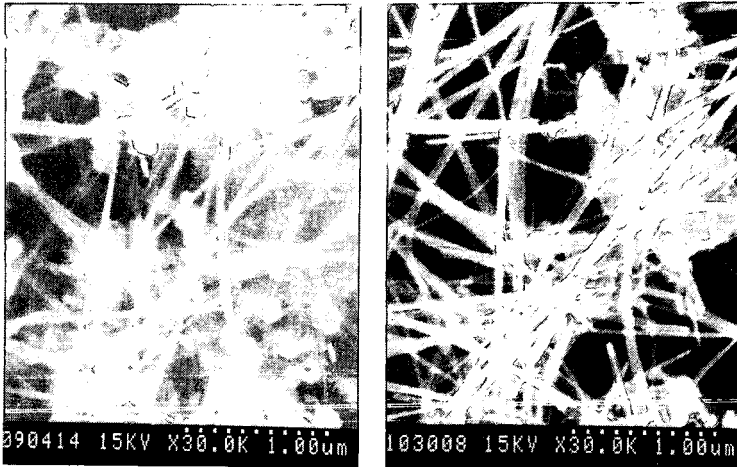


Fig.5 SEM photographs at the same position of cathode deposit at the oxidation temperature of 773 K (left; 773 K 1h, right 773 K 3h in Chemical method)

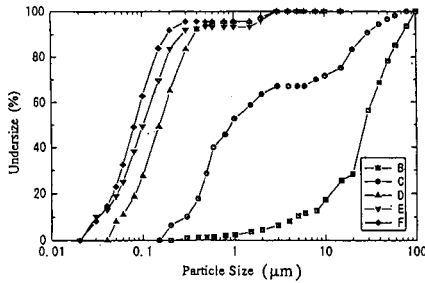


Fig.6 Particle size distribution of cathode deposit remaining in each separation step of physical method (Symbols (B-F) correspond to the symbols in Fig.2)

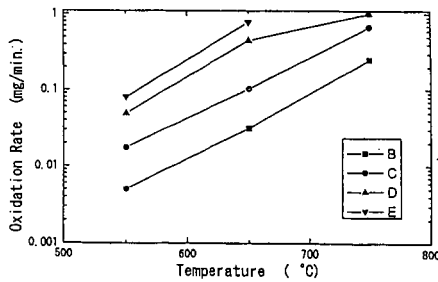


Fig.7 Oxidation rate of cathode deposit remaining in each separation step of physical method (Symbols (B-E) correspond to the symbols in Fig.2)

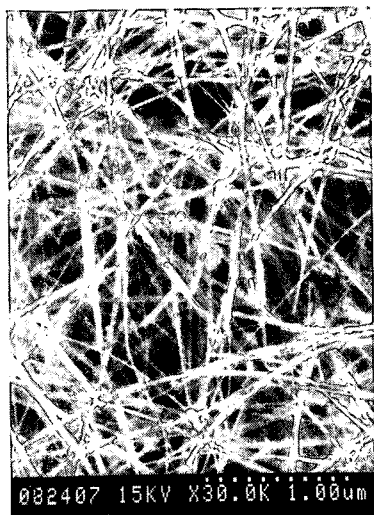


Fig.8 SEM photograph of cathode deposit after physical purification method